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The Role of Elongational Flow in Morphology Modification of Polyethylene/OMMt Nanocomposite System

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1. Introduction

The formulation of high-performance polymer based nanocomposites depend on many factors, such as polymeric matrix type, nanoparticle type, loading and morphology, affinity between the polymeric matrix and nanoparticles, presence of compatibilizer and processing conditions [1-4].
During the industrial processing the polymer based systems are subjected to two different processing flows, i.e. the shear and elongational flow. The shear flow plays a significant role in polyethylene/OMMt manufacture processing but it is not able to change the system morphology, while, the elongational flow, involved in spinning and film-blowing processing operations, can induce considerably clay morphology variations [5-13]. In order to evaluate the effect of the elongational flow on the polyethylene/OMMt system morphology, the affinity between the matrix and the OMMt particles can be considered. In particular, the presence of some compatibilizer, as maleic anhydride grafted polyethylene can modify the system affinity and subsequently, the clay morphology changes are different than the uncompatibilized system also upon the extensional flow. Nevertheless, the obtained morphology changes upon the elongational flow in the polyethylene/OMMt system, without and with good system affinity, lead to significant mechanical improvements than the unfilled systems, more larger than the simple macromolecular orientation [10, 12].
If considering, from "flow point of view", the polyethylene/OMMt system as a biphasic incompatible mixture, composed by an inorganic phase dispersed in a polymeric matrix, the applied extensional flow can be able to change strongly the clay morphology. In particular, the clay nanoparticles can be broken and/or fragmentized, dispersed and oriented along the flow direction, giving rise to flow induced intercalation/exfoliation morphology transition. Indeed, the OMMt particles can be considered as hard but breakable particles, i.e. polymeric particles in a polymeric blends, while, the conventional filler particles are elastic but unbreakable. The elongational flow leads to exfoliation of intercalated OMMt tactoids and/or to some more intercalation of the same tactoids. For the systems with good affinity

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between the components, i.e. the exfoliated clay particles are formed due to the compatibilizer loading, perpendicularly to the flow direction, some clay re-aggregation occurs, also due to action of the radial forces.
In this book chapter, will be tried to answer to two main questions, in particular: “Does the flow influence the morphology of polyethylene/OMMt nanocomposite system?” and “Which is the role of the affinity, in terms of compatibility, between the two phases?”

2. Effect of the elongational flow on the morphology modification of polyethylene/OMMt nanocomposite system

The morphology of the polyethylene/OMMTs nanocomposite system, i.e. system without any affinity between the components, upon the elongational flow, considerably changes, while, upon the shear flow, no change occurs. Indeed, as well known, the morphology of blends composed of two incompatible components is determined from the flow type. The extensional flow is able to break-up, disperse and orientate the of the dispersed system, if the viscosities of the two systems are considerably different [14-16].
In order to obtain an improvement of the OMMt morphology, also with consequent improvement in the final material performances, the study of the polyethylene/OMMt system behaviour upon the elongational flow is a critical issue. The unfilled polyethylene and OMMt filled polyethylene are subjected to the filament formation using apparatus reported in Figure 1, considering a capillary with die diameter of 1 mm and length-to-diameter, L/D=40. Before the filament formation, the polyethylene (linear low-density polyethylene, LLDPE, by Polimeri Europa, Italy) is compounded with 5 % wt./wt. organo-modified montmorillonite, OMMt (Cloisite®15A, by Southern Clay Products, USA) in a co-rotating twin screw extruder; obviously, the unfilled polyethylene is subjected to the some processing history. The formulated filaments are drawn at room temperature and the amount of drawing is characterized by the draw ratio (DRc=Lf/Lo, were Lf is the final filament length and Lo the initial length of the fibres.
The spinnability and stretchability of the polymer based systems depend on the resistance to break in the melt during the hot drawing and the melt strength, MS, and breaking stretching ratio, BSR, values can give useful information about these system capabilities. In Table 1, the values of the MS and BSR at an apparent shear rate = 60 s^{-1} are reported for the unfilled polyethylene and the OMMt filled polyethylene.
The polyethylene/OMMt system shows slightly a higher value of the melt strength and a slightly lower value of the breaking stretching ratio with respect to the unfilled polyethylene. However, the MS improvement and the relatively high value of the BSR, even if lower than the unfilled PE, indicate that the nanocomposite sample is able to filament formation as the linear low-density polyethylene sample.
In order to evaluate the mechanical behaviour as a function of the cold drawing, the filaments are subjected to the extensional flow and the dimensionless main mechanical properties, namely, elastic modulus, E, tensile strength, TS, and elongational at break, EB, are calculated and the trends in Figure 2 are reported. The dimensionless elastic modulus and tensile strength of the polyethylene/OMMt fibres are significantly higher than the unfilled polyethylene filaments. By the OMMt loading, in the isotropic state, i.e. DRc=0, compression-moulded sheets, no differences are observed in the mechanical behaviour. Some time, the dimensionless elongation at break for both systems show similar trend.

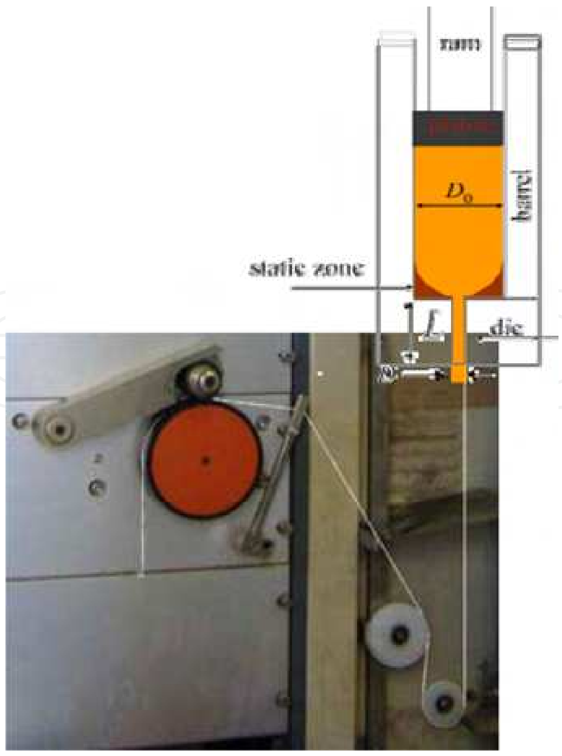


Fig. 1. Scheme of apparatus for filament formation

Sample	MS, cN	BSR
Polyethylene	3.6	39
Polythylene/OMMt nanocomposite system	4.0	30

Table 1. Melt strength, MS, and breaking stretching ratio, BSR, of unfilled Polyethylene and OMMt filled Polyethylene at apparent shear rate = 60 1/sec

The thermal analysis performed by DSC and the measurements of the total birefringence of the PE and PE/OMMt fibres at the lowest and highest draw ratio are very similar, see Table 2, suggesting similar orientation of the macromolecules for both system. However, the improvement in the mechanical behaviour of the polyethylene/OMMt system cannot be attributed only to the macromolecular orientation but can be understand and explain considering the clay morphology modification achieved upon the elongational flow.

The accurate clay morphology analysis, performed by x-ray diffraction and TEM, indicate the formation of single clay platelets and some more intercalated tactoids upon extensional flow, in particular, this phenomenon is pronounced for the highest drawn PE/OMMt fibre, see Table 3 and Figure 3. The elongational flow is able to change significantly the clay morphology, in the parallel fibre direction the interlayer distance increases from 3.30 nm for the compounded sample to 3.81 for the drawn PE/OMMt fibre at DRc=6, while, in the radial direction the morphology modification is particular, the interlayer distance slowly decreases maybe due to the some clay re-aggregation [17], due to the action of the radial fibre forces.

With the clay morphology modification upon the extensional flow, i.e. the increasing the number of the exfoliated layers and of the intercalated tactoids as a function of the draw ratio, the interface area between the polyethylene matrix and the OMMt nanoparticles increase and the mechanical improvements become much more evident than the unfilled polyethylene fibres at the same level of the macromolecular orientation.

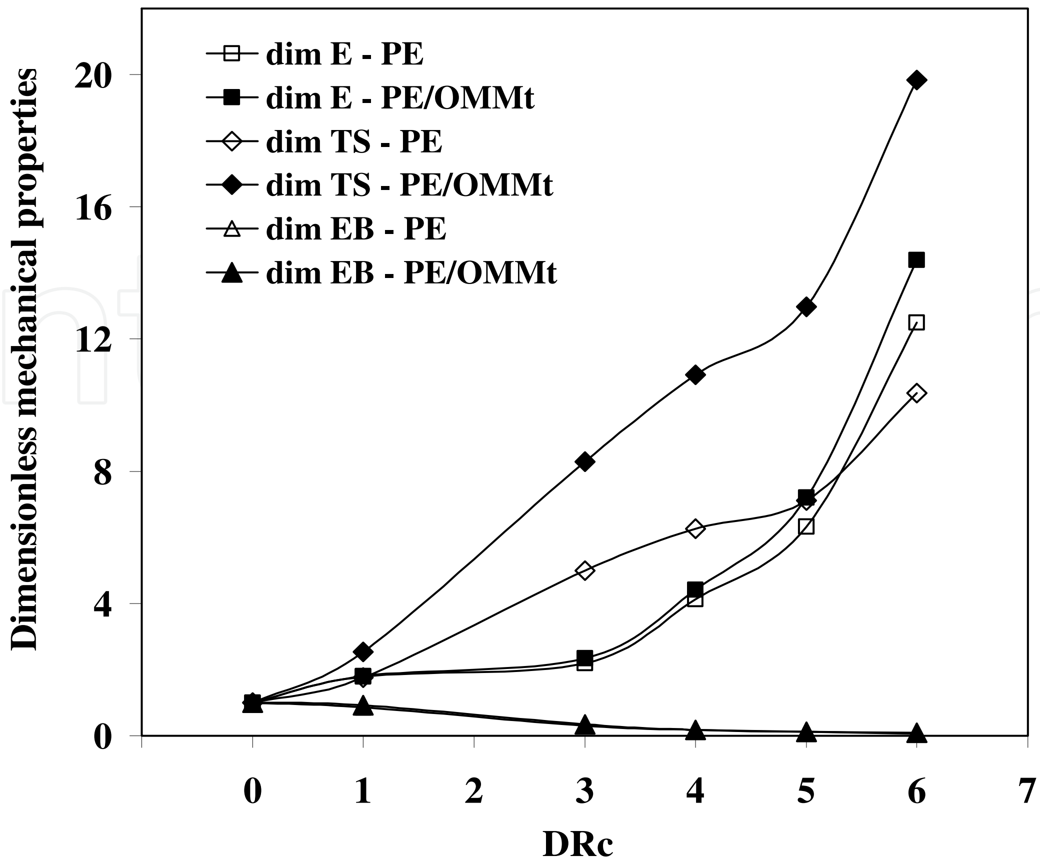


Fig. 2. Dimensionless mechanical properties as a function of the draw ratio. The dimensionless values have been calculated by dividing the values of the fibres by those of the compression-moulded sheets. *La Mantia F.P, Dintcheva N.Tz, Scaffaro R, Marino R: Morphology and Properties of Polethylene/Clay Nanocomposite Drawn Fibre. Marcomolecular Matererial and Engineering. 2008, 293, 83-91, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

Sample	Crystalline degree(*), %	Total birefringence x 10^{-3} (**)
PE fibre at DRc=1	43.4	4.1
PE/OMMt fibre at DRc=1	42.2	4.5
PE fibre at DRc=6	45.5	12.1
PE/OMMt fibre at DRc=6	44.5	12.6

(*) Crystalline degree is calculated by the thermal analyses (fusion enthalpy), using the formula:

$\alpha = \Delta H_f / \Delta H_{f100\%}$

(**) The total birefringence is calculated using the formula: $\Delta n = \Delta n_c f_c x_c + \Delta n_a f_a (1-x_c) + \Delta n_f$, where Δn_c and Δn_a are the intrinsic values of the birefringence of the crystalline and amorphous phase, f_c and f_a are the orientation factors of the two phases and x_c is the crystalline degree. The form birefringence, Δn_f, is usually considered negligible with respect to the other terms.

Table 2. Crystalline degree and total birefringence of PE and PE/OMMt fibres at lowest and highest draw ratio. La Mantia F.P, Dintcheva N.Tz, Scaffaro R, Marino R: Morphology and Properties of Polethylene/Clay Nanocomposite Drawn Fibre. Marcomolecular Matererial and Engineering. 2008, 293, 83-91, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Sample	Interlayer distance, d_{001}, nm
OMMt	3.15
Parallel direction	
compounded PE/OMMt	3.30
PE/OMMt at DRc=1	3.48
PE/OMMt at DRc=6	3.81
Radial direction	
compounded PE/OMMt	3.30
PE/OMMt at DRc=1	2.85
PE/OMMt at DRc=6	--- (*)

(*) This x-ray peak is not clearly evident

Table 3**.** Interlayer distances of different samples calculated by x-ray peak analysis using the Bragg's formula, $d_{001} = n \lambda / (2 \sin\theta)$, where n is an integer, θ is the angle in incidence of x-ray beam. *La Mantia F.P, Dintcheva N.Tz, Scaffaro R, Marino R: Morphology and Properties of Polethylene/Clay Nanocomposite Drawn Fibre. Marcomolecular Matererial and Engineering. 2008, 293, 83-91, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

4. Effect of the elongational flow on the morphology modification of polyethylene/OMMt nanocomposite system, using capillaries with different diameters and length-to-diameter ratios

In order to evaluated quantitatively the effect of the convergent extensional flow on the morphology modification of polyethylene/OMMt system, i.e. system without affinity between the components, the capillaries with different diameters and length-to-diameter ratios are used, in particular, the die diameters are Do = 1 mm, 2 mm and 3 mm, while the length-to-diameter ratios are for Do =1 mm, L/Do = 1, 4, 10, 20, 40; for Do = 2 mm, L/Do = 1, 2, 4, 40; for Do = 3 mm, L/Do = 1, 2, 4. The values of the convergent extensional stress are calculated using the Cogswell's formula [18]:

$$\sigma_{el} = 3/8\left(n + 1\right) * \Delta P_{ent} \tag{1}$$

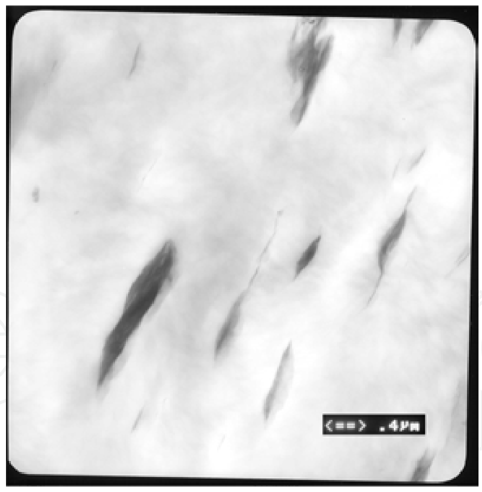
where ΔP_{ent} is the pressure drop at the entrance of the capillary and n is the flow power index.
The pressure drop was calculated adopting the followed formula:

$$\Delta P_{measured} = \Delta P_{ent} + \Delta P_{cap} \tag{2}$$

In particular:

$$\Delta P_{measured} = \Delta P_{ent} + \left(\Delta P \;/\; L \right)_{cap} * L \tag{3}$$

where $(\Delta P / L)_{cap}$ is the pressure drop for unit capillary length.
The calculated results are reported in the Table 4. Also, in order to make a correct rheological characterization, the flow curves of PE and PE/OMMt samples are measured (not reported) and the experimental data, taken with different capillary geometries, are same within the experimental error. This means that is not slip at the wall and that the Bagley correction are well evaluated.



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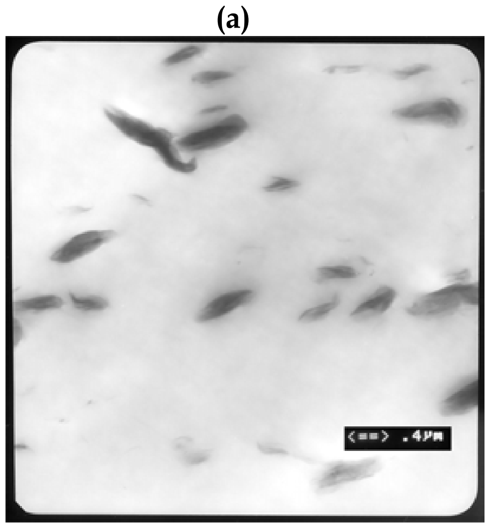

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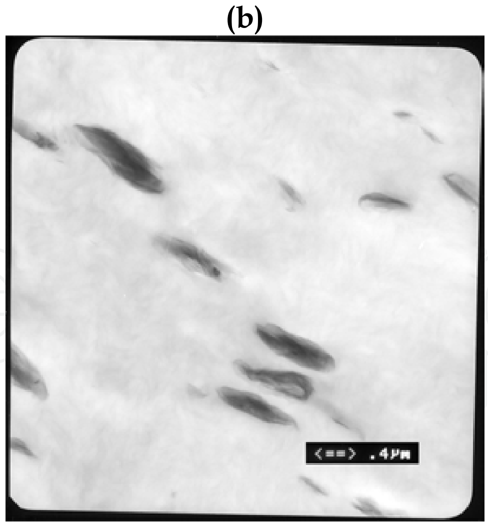


(c)

Fig. 3. TEM micrographs of (a) compounded PE/OMMt sample, (b) PE/OMMt fibre at DRc=1, (c) PE/OMMt fibre at DRc=6. La Mantia F.P, Dintcheva N.Tz, Scaffaro R, Marino R: Morphology and Properties of Polethylene/Clay Nanocomposite Drawn Fibre. Marcomolecular Matererial and Engineering. 2008, 293, 83-91, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

The convergent extensional stress, generated at the entrance of the capillary, significantly decreases with increasing of the capillary diameter and it is almost intensive to the variation of the L/D ratios. Furthermore, the values of the convergent extensional stress for the PE/OMMt sample are significantly higher than the values of the PE one. The last can be explain considering two important phenomenon, occur at the capillary entrance, in particular, some frictional interaction between the OMMt particles and some physical interaction between the OMMt nanoparticles and the matrix macromolecules. The frictional effect and the physical interaction, due to the OMMt loading, are more pronounced by the die diameter reduction and the nanoparticle morphology modification is favoured at these conditions.
The mechanical behaviour reflects the trends of the calculated convergent extensional stress, in particular, the mechanical performances increase with decrease of the die diameter due to the action of the more severe elongational flow. Also, the mechanical performances decrease with increasing of the L/D ratio, due to different macromolecular orientation.

Do = 3 mm	55	55	---
Do = 2 mm	153	161	153
Do = 1 mm	437	446	440
	L/D = 1	***L/D = 2***	***L/D = 40***

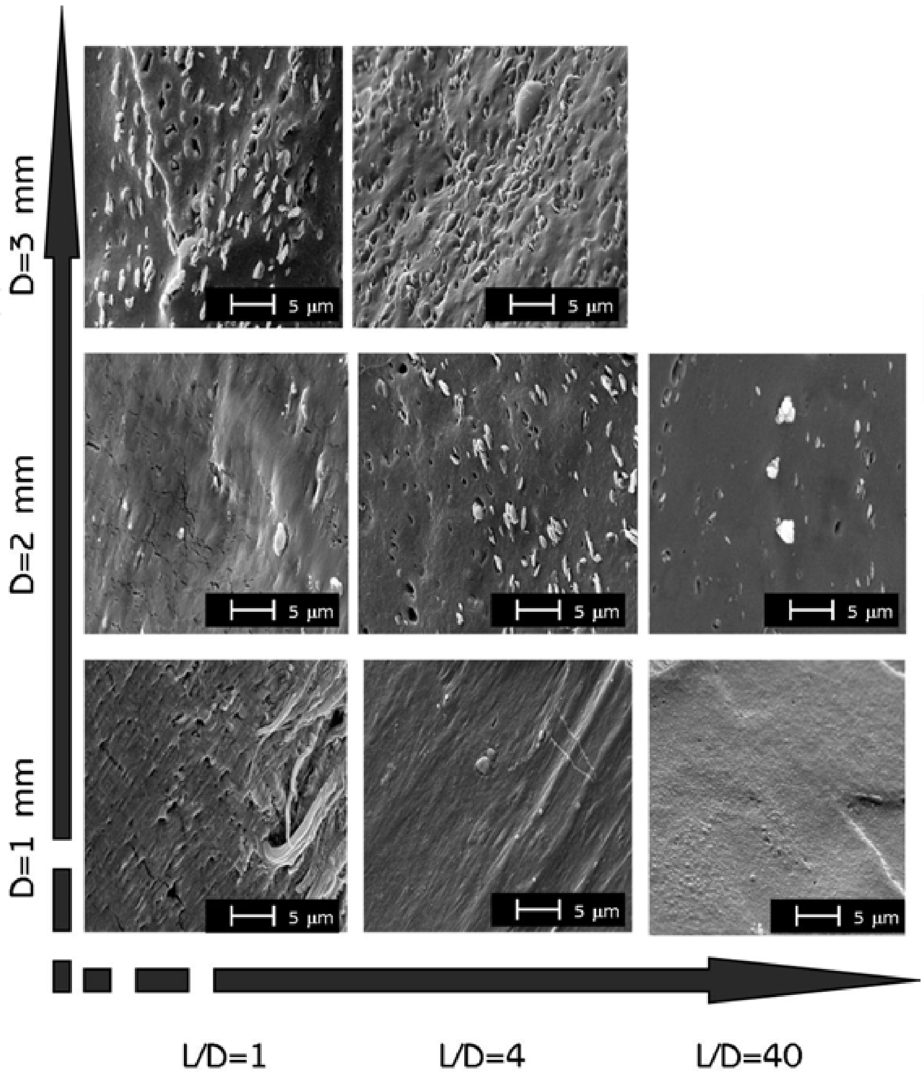
(a)

Do = 3 mm	83	84	---
Do = 2 mm	201	205	204
Do = 1 mm	737	727	727
	L/D = 1	***L/D = 2***	***L/D = 40***

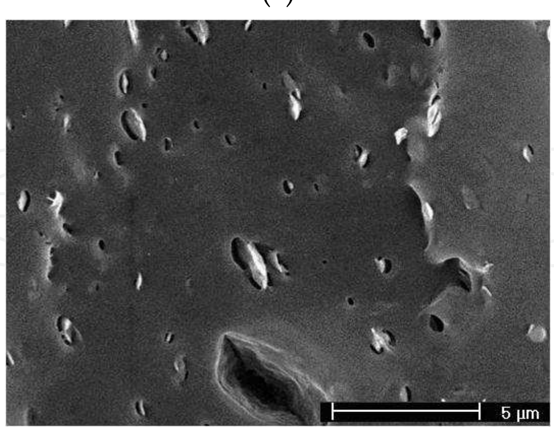
(b)

Table 4. Extensional stress values, calculated at the entrance of the capillaries of PE (a) and of PE/OMMt (b) for capillaries with different geometries. *La Mantia F.P, Marino R, Dintcheva N.Tz: Morphology Modification of Polyethylene/Clay Nanocomposite Samples under Convergent Flow. Marcomolecular Matererial and Engineering. 2009, 294, 575-581, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

The SEM morphology observations clearly indicate the formation of OMMt particles with smaller dimensions by increasing intensity of the applied convergent flow (lower values of the die diameter and L/D ratio), see Figure 4 (magnification is 10000x). The OMMt particles for the PE/OMMt prepared using capillary with Do = 1 mm and L/D= 1 are not visible at this magnification, but some time, using capillary with Do = 3 mm and L/D= 1, the particles are clearly evident, and, their dimensions are similar to the particle dimension for the compounded PE/OMMt sample. Also, no uniform OMMt particle dispersion can be noted when the sample is subjected to the weak convergent extensional stress.
The OMMt morphology modification is confirmed by x-ray analysis on the radial filament surfaces. The interlayer distances increases with the reduction of the die diameter at same L/D ratio but some time small reduction of the interlayer distances can be noted with increasing of the L/D, see Table 5. The last could be seen a contradiction (not clearly visible by SEM micrographs) but can be understand considering some re-aggregation of the OMMt particles, according to the reported in literature by Okamoto [17], due to the long residence times of the samples in the capillary, also, related to the macromolecule relaxation. It is interesting to highlight that the die diameter plays a significant role in the OMMt morphology modification, and, it is more pronounced that the role of the length-to diameter ratio.



(a)



(b)

Fig. 4. SEM micrograohs of PE/OMMt fibres (a) considering capillaries with different geometries and compounded PE/OMMt sample (b). *La Mantia F.P, Marino R, Dintcheva N.Tz: Morphology Modification of Polyethylene/Clay Nanocomposite Samples under Convergent Flow. Marcomolecular Matererial and Engineering. 2009, 294, 575-581, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

Sample	Do, mm	L/D	Interlayer distance, d_{001}, nm
OMMt	---	---	3.15
Compounded PE/OMMt	---	---	3.30
PE/OMMt	3	1	3.40
PE/OMMt	3	4	3.34
PE/OMMt	2	1	3.54
PE/OMMt	2	4	3.44
PE/OMMt	2	40	3.40
PE/OMMt	1	1	3.84
PE/OMMt	1	4	3.42
PE/OMMt	1	40	2.85

Table 5. Interlayer distances of PE/OMMt sample using capillaries with different geometries, calculated by x-ray peak analysis using the Bragg's formula, $d_{001} = n \lambda / (2 \sin\theta)$, where n is an integer, θ is the angle in incidence of x-ray beam. *La Mantia F.P, Marino R, Dintcheva N.Tz: Morphology Modification of Polyethylene/Clay Nanocomposite Samples under Convergent Flow. Marcomolecular Matererial and Engineering. 2009, 294, 575-581, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

Finally, the morphology of the PE/OMMt systems changes significantly upon the applied elongational flow. In particular, the morphology modification for the system with limited affinity between the components is more pronounced by increasing of the applied elongational stress (lower values of die diameter and L/D ratio), and, some reduction of the OMMt particle dimensions, according to the variation of the applied extensional stress can be noted.

5. Effect of the elongational flow on the morphology modification of polyethylene/compatibilizer/OMMt nanocomposite system

The loading of a commercial maleic anhydride grafted polyethylene is able to change considerably the OMMt morphology in polyethylene/compatibilizer/OMMt system due to the variation of the affinity between the polymeric matrix and the nanoparticles, as well known in literature [5-6, 19-20]. Obviously, the different started OMMt morphology by the PEgMA presence leads to different morphology modification, in particular, an almost compact delaminated OMMt structure can be obtained.

The tensile strength, see Figure 5, significantly increases, as discussed before, upon the extensional flow and this rise is more pronounced by the compatibilized loading. Also, no influences of the OMMt and campotibilizer loadings on the macromolecular orientations are observed, i.e. the thermal and total birefringence measurements show similar values for all investigated samples.

For system with greater affinity between the matrix and OMMt nanoparticles, i.e. polyethylene/compatibilizer/OMMt, the elongational flow is more efficient than the system with reduced system affinity, i.e. polyethylene/OMMt. In particular, the morphology of the OMMt nanoparticles of the PE/PEgMA/OMMt system, upon the extensional flow, shows higher level of intercalation and some exfoliation, more and more pronounced with the draw ratio. The initial intercalated OMMt morphology changes to some more intercalated and finally, at the highest anisotropic state evolves to delaminated OMMt structure. These remarks are on the basis of the morphological studies performed by x-ray diffraction and

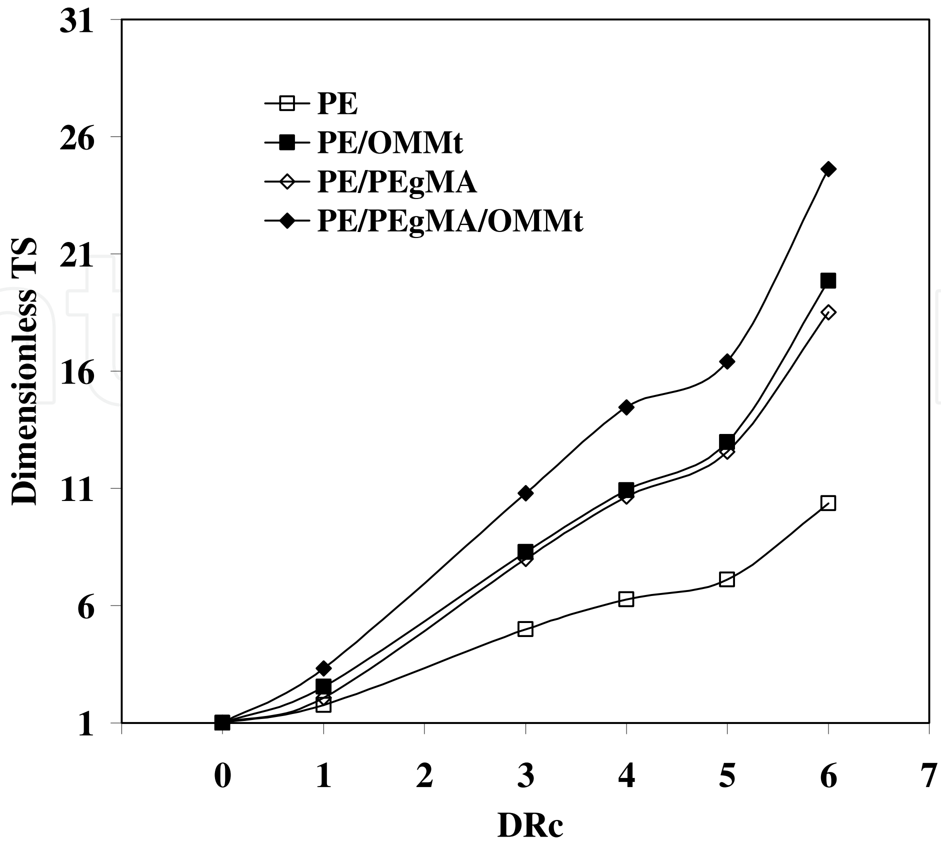


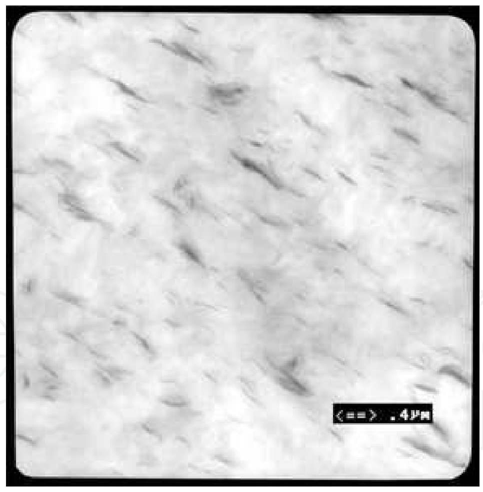
Fig. 5. Dimensionless tensile strength as a function of the draw ratio. The dimensionless values have been calculated by dividing the values of the fibres by those of the compression-moulded sheets. *Dintcheva N.Tz, Marino R, La Mantia F.P: The role of the matrix–filler affinity on morphology and properties of polyethylene/clay and polyethylene/compatibilizer/clay nanocomposite drawn fibres. e-Polymers. 2009, no. 054. Copyright e-Polymers. Reproduced with permission.*

TEM analysis. The interlayer distances for PE/PEgMA/OMMt sample are 3.42 nm for the compounded sample, 4.09 nm for the fibre at lowest draw ratio and no diffraction peak for the fibre at the highest drawing is noted. It is clear that the elongational flow, in this case, is able to change the OMMt morphology and it evolves to delaminated structured formations, confirmed also by TEM micrographs, reported in Figure 6.

6. Effect of the extensional flow on the properties of polyethylene/OMMt nanocomposite films for twist wrapping

On the basis of all the results, a practical case study for twist wrapping of PE/OMMt nanocomposite is made. As discussed before, the OMMt loading leads to more pronounced increase of the elastic modulus and tensile strength than the unfilled polyethylene sample one upon the elongational flow; together, the elongation at break and the yield strain decrease. The last means that the oriented PE/OMMt film shows improved ability in maintenance (keeping) the induced torsion deformation than the oriented unfilled PE film.

The enhanced performances of PE/OMMt film, from twist wrapping applicative point of view, are due to the significant obtained morphology modification upon the extensional flow. Some benefit synergic effect of the OMMt presence and the extensional flow on the morphology and subsequently on the applicative performances is noted.



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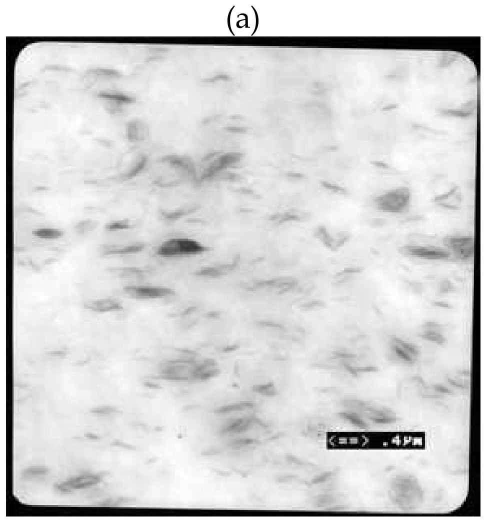

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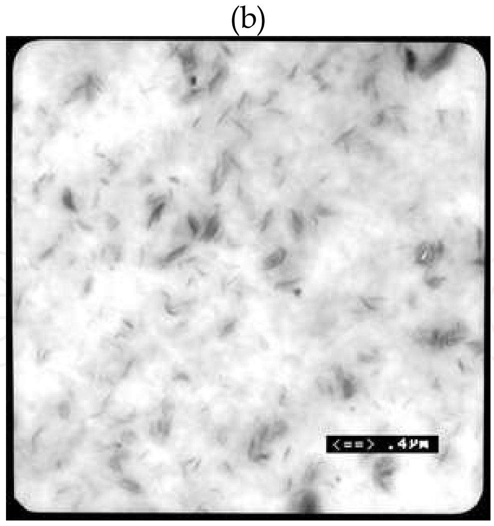

(c)

Fig. 6. TEM micrographs of (a) compounded PE/PEgMA/OMMt sample, (b) PE/PEgMA/OMMt fibre at DRc=1, (c) PE/PEgMA/OMMt fibre at DRc=6. *Dintcheva N.Tz, Marino R, La Mantia F.P: The role of the matrix–filler affinity on morphology and properties of polyethylene/clay and polyethylene/compatibilizer/clay nanocomposite drawn fibres. e-Polymers. 2009, no. 054. Copyright e-Polymers. Reproduced with permission.*

7. Conclusions

All the results agree that the elongational flow is able to change considerably the OMMt morphology. In particular, the nanoparticles can be deformed, broken and oriented along the flow direction and consequently the significant improvement in the mechanical final performances can be obtained. The improvement of the macroscopical performances cannot be attributed only to the simple macromolecular orientation but it can be explained considering the OMMt morphology modification due to two phenomena: interaction between the OMMt particles and between the OMMt particles and macromolecular matrix subjected to the elongational flow.
From an application point of view, the ability of the elongational flow in OMMt morphology modification is very important because this type of flow is involved in essential industrial processing as spinning and film-blowing. Also, the polyethylene/OMMt oriented nanocomposite film is more suitable for twist wrapping application than the unfilled polyethylene one.

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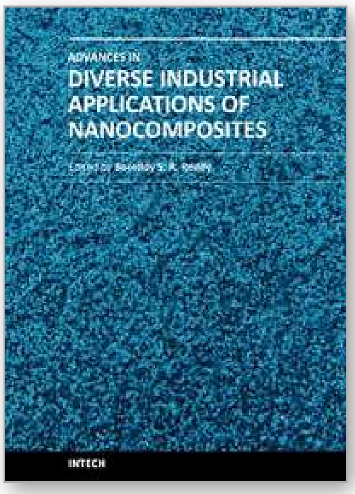

Advances in Diverse Industrial Applications of Nanocomposites
Edited by Dr. Boreddy Reddy

ISBN 978-953-307-202-9
Hard cover, 550 pages
Publisher InTech
Published online 22, March, 2011
Published in print edition March, 2011

Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.